



This invention relates to the treatment of materials in general, and in particular of substrates for electronics, optics and optoelectronics.

More precisely, the invention relates to a  
5 manufacturing process of detachable substrates, the said process comprising a surface condition adjustment treatment of at least one of two layers of material, followed by the reversible bonding of the surfaces of the two layers to constitute the detachable substrate.

10 Processes of the aforementioned type are already known.

These processes allow for the making, from two layers of material - for example semiconductor materials such as silicon - of so-called "detachable" substrates.

15 The expression "detachable" substrate designates a substrate that comprises two layers that have been bonded together, this bonding being reversible so that it is possible to separate the two layers along their bonding interface.

20 Detachable substrates thus comprise two layers made integral via a bonding interface in which the cohesion energy between the two layers is controlled so as:

• to be sufficiently great to guarantee good cohesion of the two layers forming the detachable substrate, even when this substrate is subject to thermal and/or mechanical treatments (for example thermal treatments such as high temperature annealing, mechanical treatments such as overhauling of the substrate surface),

• whilst remaining sufficiently small to offer an embrittlement zone between the two layers forming the detachable substrate, so that these two layers can be disjoined if desired (for example after the substrate has been subject to the aforementioned treatments). Typically the two layers of the detachable substrate are disjoined via a mechanical action, for example an attack by an object such as a blade.

By way of reminder, it is specified that "bonding" within the context of treatment of very thin layers as in the case of the invention, corresponds to putting into intimate contact two layers, so as to favour the creation of links, via molecular adhesion, between the bonded surfaces of the two layers.

These links may typically be hydrogen links in which the development can be stimulated via a pre-treatment of the layers that are to be bonded.

This pre-treatment, applied prior to bonding, can for example comprise a cleaning stage consisting in dipping the layers successively in:

• at least an alkaline bath. The purpose of this stage is to develop the hydrophily of the layers, by creating on the surface of the said layers OH type links.

• then an acid bath, in order to eliminate from the surface of the layers any contaminating elements (in

particular metals) that may have been brought about during the previous treatments of the layers (and in particular the alkaline bath).

5 The pre-treatment can also involve exposing the layers to a plasma for example, or other techniques known in this regard.

Moreover, it is specified that the surface condition of the layers to be bonded is, in the case of layers of material used in the manufacturing of substrates for 10 electronics, optics or optoelectronics, subject to very strict specifications.

It is thus common to have specifications concerning roughness which must not exceed a few Angstroms in rms value (root mean square).

15 It is specified that roughness is generally measured with an AFM (Atomic Force Microscope).

With this type of equipment, roughness is measured on surfaces being scanned by the tip of the AFM, ranging from  $1 \times 1 \mu\text{m}^2$  to  $10 \times 10 \mu\text{m}^2$  and more rarely  $50 \times 50 \mu\text{m}^2$ , even 20  $100 \times 100 \mu\text{m}^2$ .

And due to the surface condition of these layers, which is generally very smooth, the bonding of the layers is simply done by putting into contact the surfaces of the two layers - this putting into contact possibly being 25 complemented with a compression of the structure made of the two layers.

Now going back to the particular case of detachable substrates, it is thus known to make such substrates by applying to the surface, of at least one of the two 30 layers to be bonded, a surface condition adjustment treatment.

More precisely, such a surface condition adjustment treatment consists in applying to the surface to be treated a so-called "humid" etching, that meaning putting the surface into contact with a liquid capable of 5 attacking it, so as to adjust its roughness.

For example, the surface to be treated may be an oxide, and the liquid may be hydrofluoric acid.

The oxide of the surface may be in particular a silicon dioxide. Indeed it is specified that a preferred 10 yet not restrictive application of the invention relates to the treatment of substrates comprising a layer of semiconductor material such as silicon.

And attacking the surface with the liquid allows for the modifying as desired of the surface condition - in 15 the present case to increase its roughness to a desired level, corresponding to a surface condition which, admittedly enables the bonding with another layer, but also allows for the undoing of this bonding later on, via a mechanical action.

20 The desired roughness (typically a roughness of about 5 Angstroms rms to make a detachable substrate) is achieved by controlling in particular the length of time the surface to be treated is exposed to the liquid.

Thus, the known techniques to make detachable 25 substrates involve the attack of the surface of at least one layer by a liquid, in order to increase the roughness of this surface.

And an inconvenience relative to these known 30 techniques to make detachable substrates is that some parts of the layer to be treated that should not be attacked may happen to be exposed to the liquid.

Consequently, in the case of a layer of which only one side is to be treated, the opposite side of the layer may happen to be considerably attacked by the liquid.

Admittedly it is possible to plan for additional  
5 means to protect certain parts of the layer during humid etching.

It is thus possible to plan for these parts to be covered with a protective element, for example a varnish.

However this implies the use of specific and complex  
10 equipment.

Moreover, such means do not necessarily make it possible to systematically prevent the liquid from attacking certain parts (notably the lateral parts of the layer).

15 And the implementing of such means implies additional handling of the layers, and thus additional risks of damaging these layers (which may be extremely fragile, particularly in the case of thin layers as mentioned above).

20 Moreover, if the purpose is to control the spatial distribution of the regions of a side of a layer whose roughness is to be adjusted via the known techniques of humid etching, it is necessary to plan for relatively heavy and complex means and protocol in order to etch  
25 only the desired regions of the said side.

Indeed in this case it is necessary to cover the side of the layer of which some regions are to be etched, with a mask forming a spatial pattern which keeps free either only the regions of the layer which are to be etched (positive mask), or only the regions which are to be protected from etching (negative mask).

It is the structure made of the layer to be etched and its mask that is exposed to the humid etching. It is then necessary to remove the mask. This is achieved via chemical products and/or via the exposure to a plasma.

5 And such means to remove the mask are likely to damage the surface of the layer, and/or leave some contaminating elements on this surface.

Such contaminating elements can in particular be hydrocarbons issued from the resin having formed the mask  
10 - such hydrocarbons then constitute an obstacle to the bonding of the layer via molecular adhesion, this rendering the manufacturing of a detachable substrate from such a layer difficult.

Thus it appears that the known solutions to make  
15 detachable substrates have limitations.

A purpose of the invention is to allow for the removal of these limitations.

Another purpose of the invention is to allow for the precise controlling of the surface condition (and in  
20 particular the roughness) of layers that are to be assembled to make a detachable substrate.

In particular, it would be desirable to be able to finely adjust this surface condition, with the possibility of either selectively increasing or reducing  
25 the roughness of the surface of such layers.

Still another purpose of the invention is to allow for the local adjusting of the surface of a layer in semiconductor material, according to a set spatial pattern, without being subject to the aforementioned  
30 inconveniences.

In order to reach these goals, the invention proposes a manufacturing process of detachable substrates,

the said process comprising a surface condition adjustment treatment of at least one of two layers of material, followed by the reversible bonding of the surfaces of the two layers to make the detachable  
5 substrate, characterised in that the said surface condition adjustment treatment comprises the bombardment of the surface to be treated with clusters of at least one defined species.

Here are some preferred yet not restrictive aspects  
10 of the process according to the invention:

- the bombarded ions comprise species that are chemically inert in relation to the surface to be treated,
- the layer of material whose surface condition is to be adjusted is made of silicon or of silicon  
15 carbide, and the bombarded ions are argon or nitrogen ions.
- the said ions comprise ions that are capable of chemically reacting with the material of the surface to be treated,
- 20 • the bombardment is carried out from a plasma containing the said ions,
- the materials of the surface to be treated and the element making the plasma form one of the following pairs: (Si, SF<sub>6</sub>), (SiC, SF<sub>6</sub>/O<sub>2</sub>), (SiO<sub>2</sub>, SF<sub>6</sub>/O<sub>2</sub>), (SiO<sub>2</sub>, CHF<sub>3</sub>/SF<sub>6</sub>), (Si<sub>3</sub>N<sub>4</sub>, CHF<sub>3</sub>/O<sub>2</sub>/SF<sub>6</sub>),
- 25 • the process comprises the control of the number of ions in the clusters for the adjusting of the roughness of the surface to be treated, either with the aim of increasing or reducing this roughness,

● the said control is carried out so as to smoothen the said surface to bring its roughness to a value that enables bonding via molecular adhesion,

5 ● the surface is a negative surface of a SMARTCUT<sup>®</sup> type process that is recycled,

● the said control of the number of ions is achieved via the control of the pressure of an ion source allowing the generating of ion clusters,

10 ● the process also comprises the control of the bombardment voltage applied to the ions,

15 ● the surface to be treated is selectively and locally treated in desired zones by selectively directing towards the zones to be treated the beam of ion clusters, so as to create on this surface a pattern according to which the surface condition is selectively adjusted in the desired manner,

20 ● a focalised beam is created, comprising the ions to be bombarded as well as the monomer species of these ions, and the part of the beam comprising the ion clusters is directed towards the layer,

● the impact site of the said beam of ion clusters on the layer is controlled,

25 ● an appropriate spatial pattern is created on the surface of the layer, with a roughness that is adjusted in comparison with that of the rest of the surface of the layer, and

● patterns with variable roughness are created on the surface of the layer,

30 Other aspects, aims and advantages of the invention will become clearer upon reading the following

description, in view of the embodiments of the invention, in reference to the annexed drawings in which:

• figure 1 is a schematic diagram of an installation allowing the bombardment with ion clusters,

5 • figures 2a and 2b are graphs schematically representing the evolution of the roughness of a surface subject to a bombardment with ion clusters, under different bombardment conditions,

10 • figure 3 is a histogram illustrating the influence of the pressure associated to the generating of the ions, on the number of ions present in the clusters (it is specified that this histogram is issued from the article "Materials processing by gas cluster ion beams", Material Science and Engineering, R34, N°6, p244 (2001)),

15 • figures 4a to 4c illustrate a particular implementation method of the invention, in which a surface is selectively and locally treated so as to adjust its surface condition according to a desired pattern.

20 Now in reference to figure 1, it schematically represents an installation 10 allowing the bombarding of a layer 20 of material with a beam 30 of ion clusters.

25 Here the word "ions" can designate ions that are themselves "pure", but also species created from several ions and which are electrically charged.

Generally speaking, the "clusters" which will be spoken of below are globally ionised, that meaning that they have an electric charge other than 0. However generally speaking these clusters can further comprise 30 ions of other species, including molecules.

The layer 20 is of semiconductor material. As will be explained below, it can either be of silicon or of silicon carbide, or of another semiconductor material (SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> for example).

5 The installation 10 comprises a source 101 of pressurised gas, capable of generating a parallel beam of gas ion clusters from a plasma that is internal to the source 101.

10 It is specified that the control of the characteristics of this plasma allows for the defining of the configuration of the ion clusters, more precisely, the control of the pressure of the plasma of the source 101 allows for the controlling of the average number of ions present in the clusters, as will be detailed in 15 reference to figure 3.

And the control of the acceleration voltage allows for the controlling of the speed of these clusters.

The gas used can for example be argon or nitrogen.

20 The layer 20 corresponds to a layer whose surface condition is to be modified in a controlled manner in order to then assemble it, via bonding, with another layer (whose surface condition may also have been adjusted) so as to constitute a detachable substrate.

According to a first alternative to the invention, 25 ion clusters such as those described above are thus projected onto the surface of the layer 20, this bombardment comprising no chemical reactions.

In this case the bombardment is said to be purely "ballistic", the bombarded clusters being chemically 30 inert in relation to the material of the layer 20.

In this case, the bombarded clusters are typically made from argon or nitrogen.

According to another alternative to the invention, it is possible to bombard clusters of ions of a species, capable of chemically reacting with the material of the layer 20.

5 In this case the bombardment is said to be reactive.

And in this case, the bombarded ions can in particular be of oxygen or an oxygen compound.

In this case which includes a reactive bombardment, it is also possible to further plan for an etching plasma 10 (different from the plasma of the source 101) in a zone of the device 10 through which the ion beam will need to pass and which is located in the region of the device 10 that is immediately upstream from the layer 20.

In this particular embodiment of the invention, 15 which includes an etching plasma, it can for example be planned that the material of the surface of the layer 20 and the element making this plasma constitute one of the following pairs: (Si, SF<sub>6</sub>), (SiC, SF<sub>6</sub>/O<sub>2</sub>), (SiO<sub>2</sub>, SF<sub>6</sub>/O<sub>2</sub>), (SiO<sub>2</sub>, CHF<sub>3</sub>/SF<sub>6</sub>), (Si<sub>3</sub>N<sub>4</sub>, CHF<sub>3</sub>/O<sub>2</sub>/SF<sub>6</sub>) .

20 In this case, the ion clusters created by the source 101 chemically react with the etching plasma.

And the etching plasma itself can also chemically react with the surface of the layer, as well as the species having passed through the etching plasma with the 25 layer itself.

Going back to the description of the installation 10, the ion beam thus generated by the source 101 then passes through an accelerating chamber 102, which allows for the accelerating in the desired manner of the ion clusters of 30 the beam issued from the source 101, thanks to an acceleration electric voltage to which it is possible to give a desired value.

It is specified that in this text the "acceleration voltage" of the source 101 actually corresponds to the acceleration voltage of this accelerating chamber 102.

This beam then passes through a beam-creating 5 electromagnetic structure 103 which allows for the adjusting of the characteristics of the magnetic field of the beam (collimation, focalisation...), via the application of electromagnetic fields with desired characteristics.

10 The beam then passes through a magnet annular structure 104 which also allows for the creation of a field with controlled characteristics, in order to selectively deviate the charged species of the ion beam.

Indeed it is specified that the beam issued from the 15 accelerating chamber 102 and the electromagnetic structure 103 comprises ion clusters of the bombarded species, but also molecules which are electrically neutral (in particular monomers of the bombarded species).

The trajectory of the different elements of this 20 beam is represented as being strictly rectilinear on the schematic representation in figure 1.

Actually, these trajectories are not rectilinear, the radius of curvature of the trajectory depending on the mass of the ions and of the different elements of the 25 beam.

And by precisely controlling the characteristics of the magnetic field generated by the magnet annular structure 104, it is possible to selectively deviate only the desired ion clusters towards the opening of a screen 30 106, as the other constituents of the beam do not pass through this opening, being stopped by the screen 106.

It is specified that the structure 103 and the structure 104 can be one and the same.

An electrical neutralising structure 105 is also provided.

5 A screen 106 with an opening 1060 is, as has been said, positioned so as to only let through the part of the beam that comprises the desired clusters, so that the latter can have an impact on the layer 20 located behind the opening 1060.

10 The screen 106 and its opening 1060 constitute fixed parts of the device.

15 And the part of the beam which passes through this opening to have impact on the layer 20 corresponds to a focalised beam, following the passing through of the means 103.

20 Hence, the layer 20 only receives the impact of the beam of ion clusters over a basic surface of very small dimensions (the section of the beam passing through the opening 1060 has a width of about one or a few millimetres).

As for the layer 20, it is mounted on a movable support 107 whose displacements within the plane perpendicular to the beam, are controlled.

25 It is thus possible to define with great precision an etching pattern of the ion clusters on the surface of the layer 20, by displacing this layer according to a desired trajectory using the means 107, so that the impact site of the ion clusters on the layer 20 traces a special pattern. This aspect will be further considered  
30 later.

A screened room 108 is located behind the layer 20 and the means of displacement 107, facing the impact zone of the beam on the layer 20.

This screened room 108 is connected to means 109 of  
5 determining the dose of species received by the layer 20.

The bombardment of the layer 20 with ion clusters of desired characteristics thus allows for the adjusting of the roughness of the surface of this layer, in view of constituting a detachable substrate.

10 It is to be noted that, in comparison with the known techniques to modify the surface condition via humid etching, the bombardment with ion clusters does not present the inconveniences described in the introduction of this text.

15 In particular, no "leak" or contamination is to be feared, as, first of all, the technique used here to modify the roughness of the surface of the layer belongs to "dry" etching techniques, and not "humid": here the layer 20 does not come into contact with liquids.

20 Moreover, the bombardment technique with ion clusters used in the context of this invention allows, as has been said, to very precisely control the impact zone of the ion clusters on the layer 20.

This remains true even in the case where the layer  
25 is not displaced, as the dimensions of the section of the beam that has impact on the layer are very small, as already mentioned.

And the fact of carrying out this bombardment not simply with ions but with clusters of ions, allows for  
30 great freedom in the adjusting of the surface roughness of the layer 20.

More precisely, it is possible to selectively reduce, or increase, the surface roughness of the layer 20.

Indeed it has been observed that, depending on the characteristics of the bombardment with ion clusters, it  
5 is possible to either increase or reduce this roughness.

More precisely, in reference to figure 2a, it schematically represents several curves C1 to C5 substantially rectilinear, that translate the evolution of the roughness R of the surface of the layer 20, versus  
10 the evolution of the voltage V applied to the beam inside the accelerating chamber 102.

Each of these curves in figure 2a corresponds to a bombardment condition in which the ion clusters mainly comprise a respective number of ions.

15 Indeed, the control of the bombardment parameters allows to determine the number of ions present in the clusters bombarded on the layer 20.

It is specified that the main parameter that controls the number of ions present in the clusters is  
20 the pressure inside the ion source 101.

Thus, by controlling this pressure of the source 101, the number of ions in the clusters is also controlled.

This is illustrated on the histogram in figure 3.

Indeed this figure represents several curves A1, A2,  
25 A3, A4.

Each of these curves represents the size repartition of the ion clusters, for a given pressure of the source.

The size of the clusters is represented by the number of atoms per cluster (upper horizontal scale),  
30 which here varies from 0 to 3000 atoms per cluster.

The lower curve A1 is associated with a pressure of 760 Torr, the curve A2 with a pressure of 2300 Torr, the

curve A3 with a pressure of 3000 Torr, the curve A4 with a pressure of 3800 Torr.

It can be observed that the peak of these curves - which corresponds to the most common cluster size for the 5 pressure in question - has greater values as the pressure increases.

Hence it can be observed that the number of ions present in each cluster lies around an average number of ions per cluster, this average number being designated N.

10 And it is thus possible, by controlling the pressure of the ion source, to control this value of N.

Each curve in figure 2a thus corresponds to a different value of N: the value of N increases when changing curve, from C1 to C2, to C3, to C4, to C5.

15 The curve C1, the highest, corresponds to a bombardment with individual ions, that meaning under conditions where N equals 1.

Under these conditions, it can be observed that, as the acceleration voltage of the ions of the beam 20 increases, the surface roughness of the layer 20 subject to the bombardment with "clusters" each made of a single ion, increases considerably.

Indeed under these bombarding conditions, the ions individually bombarded on the layer provoke major damage 25 to the surface structure of the layer.

The curve C2, immediately below the first curve, corresponds to bombardment conditions under which N has a value greater than 1.

In this case it can be observed that the same 30 increase in acceleration voltage does not result in as great an increase of the surface roughness, even though this roughness increases.

The next curve C3 illustrates a low increase of the roughness for the same increase in the voltage V.

And the curve C4, which corresponds to bombardment conditions under which the bombarded clusters comprise a 5 rather large number of ions, illustrates a constant roughness despite the increase in the acceleration voltage V.

Indeed, when the ion clusters comprise a number N of ions greater than a given threshold, the slope of the 10 evolution curves  $Rf(V)$  becomes nil, under certain conditions. This threshold notably depends on the starting surface condition of the layer, prior to bombardment.

And when the number N continues to increase, the 15 bombardment does not increase the surface roughness of the layer 20, but rather reduces it by smoothing this surface.

This incidence is illustrated by the curve C5.

By adjusting the bombardment conditions - and more 20 precisely the number of ions present in the clusters - it is thus possible to adjust in the desired manner the surface condition of the layer 20:

- by increasing to a greater or lesser extent the surface roughness of this layer,
- 25        • or even by reducing this roughness. This is useful in the cases where the surface of the layer 20 has a high roughness at the start of bombardment.

It thus appears that two parameters defining the bombardment conditions have a major influence on the 30 progression of the process:

• the pressure associated with the generating of the ions allows for the controlling of the number of ions present in the clusters,

5 • the acceleration voltage allows for the controlling of the speed of the clusters, and also has an influence as described in reference to figures 2a and 2b.

This influence can be exploited by programming bombardment sequences during which different regions of the layer 20 are subject to bombardments with clusters 10 comprising different numbers of ions, so as to selectively adjust in a desired manner the surface roughness of these different regions.

For this purpose, the means of displacement 107 will be programmed to displace the layer 20 in conjunction 15 with changes to the parameters allowing to modify the value of N, during the different successive stages of a given bombardment of the layer.

Now in reference to figure 2b, it again represents the evolution of the surface roughness R of the layer 20 20 subject to a bombardment with ion clusters comprising an average number N of ions which can vary (here again corresponding to different curves in this figure), versus the acceleration voltage V.

This figure includes the curves C1 to C5 of figure 25 2a.

However figure 2b also shows another set of curves C'1 to C'5, which evolve according to the same general logic as the curves C1 to C5 (increase in the number N from curve C'1 to curve C'5, for the same starting layer 30 20 and the same bombarded ions).

It can be observed on the curves C'1 to C'5 that, contrary to the curves C1 to C5, the increase in the

number N does not result in a reduction of the surface roughness of the layer 20.

It is specified that the curve C'5 corresponds to a number N that is very large, which can be assimilated 5 with an infinite value of N.

It can be noted that when the surface condition of the layer 20 already corresponds to a low roughness (curves C'1 to C'5), it becomes impossible to smoothen the surface of this layer by increasing N.

10 Hence, starting with a layer whose surface roughness is relatively important, it is possible to selectively increase, or reduce, this roughness.

An interesting application of this consists in using 15 as layer 20 wafers whose surface condition is incompatible with bonding via molecular adhesion (roughness greater than a value of about 5 Angstroms rms), to treat certain regions of these wafers so as to smoothen them and bring their roughness to a value that enables such bonding.

20 In particular this allows for the recycling of negatives issued from a SMARTCUT<sup>®</sup> type process, by reusing them.

And still in this case, it is possible to use layers 25 constituted from a wafer whose intrinsic surface condition is incompatible with bonding (SiC, III-V). Instead of proceeding with the complete polishing of such a wafer, a bombardment with clusters comprising a rather large number N of ions will make it possible to smoothen the surface of the wafer.

30 Moreover, this smoothing can be very precisely controlled, both in terms of final roughness and in terms

of creating a spatial pattern with more or less smooth regions in view of bonding.

However if the starting surface condition of the layer 20 is inferior to a given threshold  $R_0$  (which 5 depends among other things on the nature of the material of the layer and of the bombarded species), it will only be possible to increase this roughness.

Indeed, if the starting point of the curves C'1 to C'5 happened to be below the threshold  $R_0$  (whereas it is 10 situated at the level of this threshold in figure 2b), it would not even be possible to retain this starting low roughness by proceeding with a bombardment of the surface: even a bombardment with a very great value of N would result in an increase of the roughness.

15 Now in reference to figures 4a to 4c, they schematically represent layers 20 having been subject to a bombardment with ion clusters such as described above, during which the roughness of certain regions of the surface of the layer has been selectively modified.

20 Figure 4a thus represents a layer on the surface of which a ring has been created with a roughness lower than that of the rest of the surface, so as to obtain a greater mechanical stability on this ring at the time of assembling the layer 20 with another layer (homogeneously 25 smooth for example).

Thanks to the programming of the means of displacement 107, it is possible to create on the surface of the layer, any other desired pattern. Figures 4b and 30 4c thus respectively represent a layer 20 with a grid pattern, and with a paved pattern, with a roughness lower than that of the rest of the surface of the layer.

And by controlling the number  $N$  of ions in the bombarded clusters in conjunction with the displacement of the layer 20, it is thus possible to create any pattern, including with several levels of roughness 5 selectively distributed over different desired regions of the surface of the layer.

It is then possible to create patterns with variable roughness, to constitute detachable substrates whose distribution of roughness over the surface is perfectly 10 controlled.

The expression "pattern with variable roughness" designates a pattern of which different zones may have different roughness.

It is to be noted that the implementation of the 15 invention thus allows for the very fine controlling of the levels and distributions of roughness on the surface of a layer from which a detachable substrate is to be created after the reversible bonding via molecular adhesion with another layer (whose roughness may have 20 been adjusted if necessary).

It is also to be noted that the fact of proceeding with a bombardment with ion clusters only modifies the surface of the layer 20, no subsurface damage being engendered by such a bombardment. In this regard 25 reference can be made to the article "Substrate smoothing using gas cluster ion beam processing" by Allen and al., Journal of Electronic Materials, Vol.30, N°7, 2001.